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Formation of a new class of 7π radicals *via* sterically induced P–P bond cleavage of the dimers $[(CH)_2(NR)_2P]_2$†

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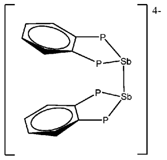
The 2c–2e$^-$ P–P bonded dimers $[(CH)_2(NR)_2P]_2$ dissociate in solution to give the persistent new 7π radicals $[(CH)_2(NR)_2P]^\bullet$, which are isoelectronic with the well known S/N thiazolyl radicals.

The pursuit of stable molecules containing unpaired electrons has been of interest to researchers for many years, and is at the forefront of the development of new magnetic materials.[1] Although the existence of main group radicals has been known since the 1800s, it has only been since the 1960s that persistent compounds of the heavier group 14 and 15 elements containing unpaired electrons have been isolated and characterised.[2] Two main strategies have been employed to stabilise main group radicals. One approach has been by the use of π-delocalisation of the electron over several centres, combined with the incorporation of electronegative elements, to form unreactive, low-energy singly-occupied molecular orbitals (SOMO) as seen in the extensive classes of 7π S/N and Se/N radicals.[3] In addition, kinetic stabilisation has been used in the form of highly bulky steric groups to shield the reactive radical centre against attack by other molecules or from forming dimers.[2] In fact, it is this tendency for formation of covalently bonded spin-paired dimers that often represents the biggest obstacle to the isolation of radicals.[1]

The chemistry of persistent radicals of the heavier elements of group 15 (notably phosphorus), although less well developed than those based on group 16, is characterised by a high degree of structural and chemical diversity, including radical centres based on both P(III) and P(V).[2,4] These include examples of pure σ-radicals, where the unpaired electron is localised in an orbital on a phosphorus centre, as well as π-based systems where spin density is extended over several nuclei. Several classes of phosphorus-based radicals have been studied, including phosphinyls $[R_2P]^\bullet$,[5] diphosphanyls $[R_2PPR]^\bullet$,[6] 1,3-diphosphaallyls $[(RP)_2CR]^\bullet$,[7] and phosphoranyls $[R_4P]^\bullet$.[8] By far the most studied of these are the phosphinyl and related arsinyl systems, and in a few cases the structure of the free radical in the vapour phase has been determined by electron diffraction methods.[9,10] Structural studies have suggested that dissociation of the group 15 dimers R_2EER_2 (E = P, As) is largely driven by release of steric strain between the bulky silyl substituents, even in cases where a short (presumably strong) E–E bond is present.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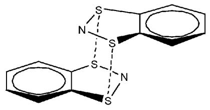
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Our recent report of the synthesis of the σ-bonded Sb–Sb bonded anion $[1,2\text{-}C_6H_4P_2Sb]_2^{4-}$ (**A**),[11] which is valence-isoelectronic with the π-bonded benzo-1,3-dithia-2-azolyl radical dimer (**B**),[12] suggested that a broad class of new radicals may be obtainable involving valence-isoelectronic combinations of various main group elements. We show in this paper that a new family of P-based 7π radicals is readily accessible *via* low-energy P–P bond cleavage, driven by a combination of steric stabilisation and electronic delocalisation within their C_2N_2P frameworks. The key precursors to the new 7π radicals are the P–P bonded compounds **1** obtained in crystalline form by reduction of the known *p*-chloro-diazaphospholenes $(CH)_2(NR)_2PCl$[13] with Mg powder in thf (Fig. 1).‡ Importantly, the stability and reactivity of compounds of this type have not been investigated previously, although the high reactivity of P–P bonds in the unsymmetric species $(CH)_2(NR)_2P\text{–}PR'_2$ has been noted.[14] Significantly, however, the potential intermediacy of $[(CH_2)_2(NR)_2P]^\bullet$ radicals appears to have been overlooked in this case.

All three compounds **1a–c** exist as *trans*-oid dimers in the solid state (Fig. 2) in order to minimise steric repulsion between the bulky organic groups.§ A large increase in the P–P bond length is observed on moving from 2.2439(8) Å in **1a** (R = ^{t}Bu) to 2.324(2) Å in **1b** [R = Mes (mesityl)], to mean 2.33 Å in **1c** [R = Dipp (2,6-diisopropylphenyl)]; *cf.* 2.21 Å

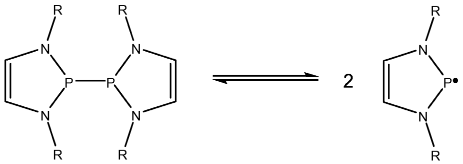

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Fig. 1 Dissociation of diazaphospholene dimers into monomeric 7π radicals. **1a** (R = ^{t}Bu), **1b** (R = Mes), **1c** (R = Dipp).

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† Electronic supplementary information (ESI) available: EPR spectra for **1b** and **1c**; calculated bond lengths, angles and SOMO of the model heterocyclic $C_2H_2(NMe)_2P^\bullet$ system by DFT at increasing levels. CCDC reference numbers 707574 (**1a**), 707575 (**1b**) and 707576 (**1c**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b821241d

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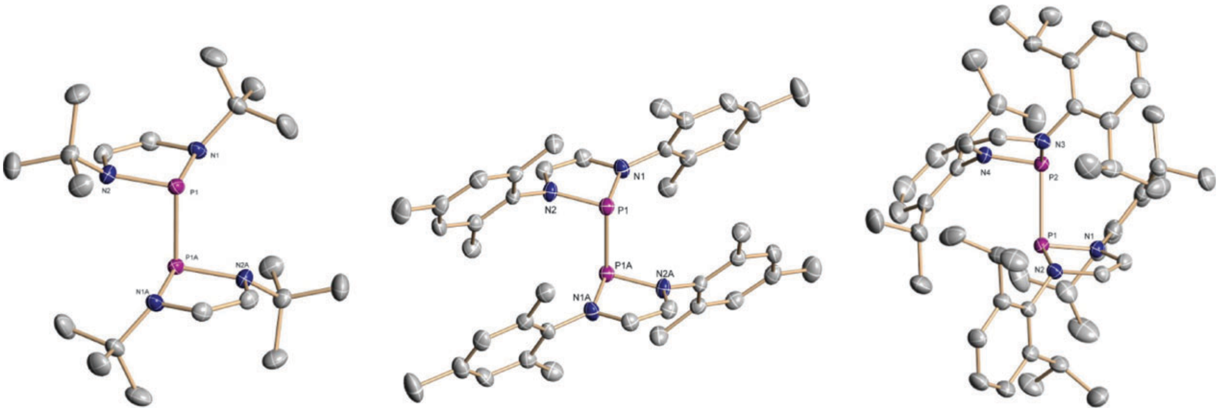

Fig. 2 Solid-state structures of **1a**, **1b** and **1c**. Thermal ellipsoids are drawn at the 50% level. H-atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **1a** P(1)–P(1A) 2.2439(8), P(1)–N(1) 1.7388(11), P(1)–N(2) 1.7394(8), N(1)–C(1) 1.4217(10), N(2)–C(2) 1.4144(11), C(1)–C(2) 1.3383(13); N(1)–P(1)–N(2) 94.28(4), N(1)–P(1)–P(1A) 94.33(4), N(2)–P(1)–P(1A) 94.24(4), C(1)–N(1)–P(1) 106.31(6), C(2)–N(2)–P(1) 106.59(6), C(2)–C(1)–N(1) 115.22(7), C(1)–C(2)–N(2) 115.34(7); **1b** P(1)–P(1A) 2.3240(16), P(1)–N(1) 1.728(2), P(1)–N(2) 1.727(2), N(1)–C(1) 1.412(3), N(2)–C(2) 1.411(4), C(1)–C(2) 1.324(4); N(2)–P(1)–N(1) 89.76(11), N(2)–P(1)–P(1A) 97.44(9), N(1)–P(1)–P(1A) 97.95(9), C(1)–N(1)–P(1) 109.59(18), C(2)–N(2)–P(1) 110.02(19), C(2)–C(1)–N(1) 113.6(3), C(1)–C(2)–N(2) 112.9(3); **1c** (mean distances and angles) P–P 2.33, P–N 1.73, N–C 1.43, C–C 1.33; N–P–N 90.91, N–P–P 96.27, 114.70, C–N–P 109.88, C–C–N 113.79. Symmetry transformations used to generate equivalent atoms: **1a**: $-x + 1, -y + 1, -z + 1$, **1b**: $-x, -y, -z$, for **1c** only one of the molecules in the ASU is shown and disordered lattice solvent was omitted for clarity.

mean value observed for P–P single bonds in the literature.[15] These P–P bond lengths represent relatively long P–P bonds, although are exceeded by those present in the highly polarised, unsymmetrical systems reported by Gudat *et al.* [up to 2.484(1) Å] which utilised the same heterocyclic C_2N_2P ring systems.[14] In addition to the lengthening of the P–P bond, other structural distortions arise in order to minimise the steric clash between the $(CH)_2(NR)_2$ ring units. Most obvious are the puckering of the $(CH)_2(NR)_2$ ring units, and the bending of their organic substituents out of the heterocyclic ring plane and the twisting of the P–P bond in the most sterically congested dimer **1c** (*ca.* 111°) away from the centrosymmetric arrangements observed in **1a** and **1b** in order to accommodate the very large Dipp groups.

As a result of the presence of P–P bonded arrangements, **1a–c** are all EPR-silent in the solid state. No solution EPR signal could be detected for **1a** in toluene at room temperature. However on increasing the temperature to 353 K the colour of the solution changed from colourless to faint yellow, signalling the shifting of the monomer–dimer equilibrium in favour of the radical monomer form. The EPR spectrum of **1a** recorded at 353 K (Fig. 3) shows a doublet further split into 1 : 2 : 3 : 2 : 1 quintets ($g = 2.00088$), consistent with hyperfine coupling to one phosphorus [$A(^{31}P) = 41$ G] and two equivalent nitrogen [$A(^{14}N) = 5.8$ G] nuclei. Couplings to phosphorus are lower and to nitrogen higher than observed in non-cyclic phosphinyls [typically $A(^{31}P) = 63–108$ G, $A(^{14}N) = 3.7–5.1$ G],[1] corresponding to a delocalisation of the unpaired electron about the π-system of the heterocyclic framework rather than being overwhelmingly P-based. No ^1H coupling was observed, either to the organic substituents (^{t}Bu) or to heterocyclic C–H atoms. The longer, weaker P–P bond in **1b** permitted a similar spectrum to be observed at the lower temperature of 315 K [$g = 2.01775$, $A(^{31}P) = 40$ G, $A(^{14}N) = 5.2$ G] whilst **1c**, having the bulkiest steric groups and longest P–P bond, showed significant dissociation into monomeric radicals at room temperature, as shown by EPR spectroscopy [$g = 2.0248$, $A(^{31}P) = 42$ G, $A(^{14}N) = 5.4$ G, see ESI†]. It is worthwhile to compare EPR spectra we have obtained with those reported by West *et al.* for a series of structurally similar heterocyclic radicals $(CH)_2(N^tBu)_2M–R$, where the P atom in **1a** has been substituted by M–R groups (M = Si or Ge).[16] Seven-line EPR spectra with strong coupling to heterocyclic C–^{1}H nuclei were reported. However, anomalously no coupling to ^{29}Si was observed for the $(CH)_2(N^tBu)_2Si–R$ radical, even though calculations predicted a large hyperfine coupling to this nucleus.

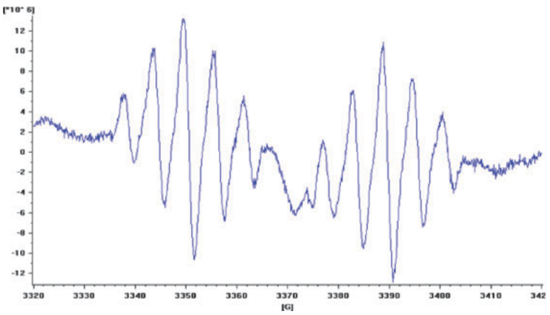

Fig. 3 EPR spectrum of **1a** in toluene at 353 K.

Density functional theory (DFT) calculations were undertaken to gain insight into the nature of the frontier orbitals and the dimerisation energy of these species.[17] The model heterocyclic $(CH)_2(NMe)_2P^\bullet$ system was geometry optimised at the double-zeta UB3LYP/6-31G, UB3LYP/6-31G* and triple zeta UB3LYP/6-311G and UB3LYP/6-311G* levels in order to assess the basis set dependence of the calculations. Reassuringly, the nature of the frontier orbitals was not affected on increasing the size of the basis set. The frontier orbitals obtained at the 6-31G level for $(CH)_2(NAr)_2P^\bullet$ (Ar = 2,6-$Me_2C_6H_3$), models for **1b** and **1c**, are also similar to those determined for $(CH)_2(NMe)_2P^\bullet$ (Fig. 4). The SOMO show that the majority of the unpaired electron density lies on the heterocyclic C_2N_2P ring, broadly consistent with EPR studies

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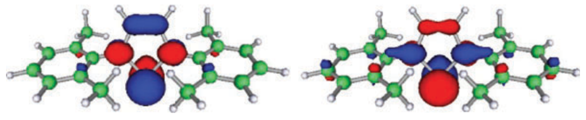

Fig. 4 SOMO (left) and LUMO (right) of **1c**.

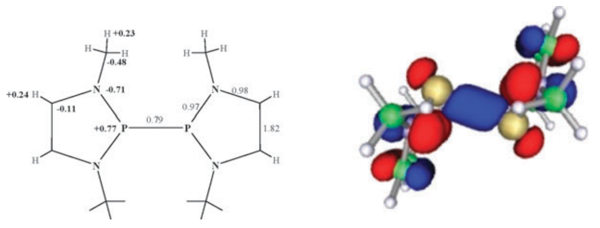

Fig. 5 (Left) NBO charges (bold) and bond orders in the $[(CH)_2(NMe)_2P]_2$ dimer, and (right) bonding interaction between radicals in the HOMO.

of **1a–c** discussed previously. Calculations on the dimer $[(CH)_2(NMe)_2P]_2$ at the B3LYP/6-31G level revealed it to be a minimum on the potential energy surface and showed a small dimerisation energy (ΔE) of $\sim$3 kJ mol^{-1}, perhaps lower than expected considering the elevated temperatures required to detect EPR signals. Accurate estimates of dimerisation energies of radicals are, however, difficult to obtain¶ (being highly dependent on the basis set used) though the observation of a stable dimer on the potential energy surface is significant. Solution is viable at accessible temperatures. The calculated parameters are consistent with a weakly σ-bonded dimer formed through a *trans*-cofacial π*–π* interaction equivalent to a 2c–2e$^-$ P–P bond involving p-orbitals (Fig. 5).

In conclusion, applying simple isoelectronic principles has allowed us to predict homolytic cleavage of the P–P bonds in dimers of the type $[(CH)_2(NR)_2P]_2$ and to establish a new class of 7π radicals.

Notes and references

‡ All manipulations were performed using Schlenk-line techniques under an atmosphere of dry argon. Chloro-diazaphospholenes were synthesised according to published procedures.[13b] The synthesis of **1a** is described below. Compounds **1b** and **1c** were obtained in crystalline form using a similar procedure, but have only currently been obtained in low yields. Optimised syntheses of both will be published in a full paper on this work in due course. Synthesis of **1a**, [1,1′,3,3′-tetra-*tert*-butyl-1,1′,3,3′-tetrahydro-2-2′-bi(1,3,2-diazaphosphole)]: Mg powder (21 mg, 0.85 mmol) was added to a solution of 1,3-bis(*tert*-butyl)-2-chloro-1,3,2-diazaphospholene (200 mg, 0.85 mmol) in 5 ml thf, and the mixture stirred overnight at room temperature. The volume of solvent was then reduced to approx. 1 ml and the mixture left to crystallise at −20 °C for 1 d. The pale yellow crystals were filtered and dried *in vacuo*. Yield 66 mg, 39%. ^{1}H NMR (500 MHz, C_6D_6): δ = 6.02 (t, 4H, CH═CH, J_{H-P} = 1.9 Hz), 1.33 (s, 36H, CH_3); ^{13}C NMR (500 MHz, C_6D_6): δ = 121.19 (s, C═C), 54.15 (t, N–C–Me$_3$, J_{C-P} = 7.7 Hz), 30.22 (t, CH_3, J_{C-P} = 3.9 Hz); ^{31}P{^{1}H} NMR (400 MHz, C_6D_6) δ = 80.8.

§ Crystal data for **1a**: Empirical formula $C_{20}H_{40}N_4P_2$, FW = 398.50, crystal system triclinic, space group $P\bar{1}$, a = 6.3138(1), b = 9.8033(2), c = 10.3563(2) Å, α = 73.7030(8), β = 72.8375(8), γ = 87.2143(9)°, V = 587.45(2) Å^3, Z = 1, ρ_{calcd} = 1.126 Mg m^{-3}, μ(Mo-Kα) = 0.196 mm^{-1}, reflections collected 12 404, independent reflections 4070 [R_{int} = 0.022]. R_1 = 0.0285, wR_2 = 0.0802. **1b**; Empirical formula $C_{40}H_{48}N_4P_2$, FW = 646.76, crystal system triclinic, space group $P\bar{1}$, a = 8.6059(3), b = 10.2485(4), c = 10.8287(4) Å, α = 85.8725(16), β = 74.5382(17), γ = 73.0208(14)°, V = 880.36(6) Å^3, Z = 1, ρ_{calcd} = 1.220 Mg m^{-3}, μ(Mo-Kα) = 0.158 mm^{-1}, reflections collected 9748, independent reflections 3565 [R_{int} = 0.067]. R_1 = 0.063, wR_2 = 0.0135. **1c**; Empirical formula $C_{53}H_{74}N_4O_{0.25}P_2$, FW = 833.10, crystal system triclinic, space group $P\bar{1}$, a = 12.1056(1), b = 20.2299(2), c = 21.6313(2) Å, α = 72.598(1), β = 77.804(1), γ = 81.880 (1)°, V = 4923.51(8) Å^3, Z = 4, ρ_{calcd} = 1.124 Mg m^{-3}, μ(Mo-Kα) = 0.127 mm^{-1}, reflections collected 57 801, independent reflections 17 212 [R_{int} = 0.0337]. R_1 = 0.0378, wR_2 = 0.0956. Data were collected on a Nonius KappaCCD diffractometer at 180(2) K (**1a**, **1b**) and 150(2) K (**1c**), solved by direct methods and refined by full-matrix least squares on F^2.[19]

¶ Calculations by Oakley on the radical $HCN_2E_2^{\bullet}$ (E = S, Se) have shown that accurate estimates of dimerisation energy are not easily obtained even using large basis sets or additional correlation functions.[18] In addition, these are gas-phase calculations which neglect solvation effects.

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